Coordination Chemistry Reviews, 100 (1990) 267–292
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE ROLE OF GROUP 14 ELEMENT CARBENE ANALOGUES IN TRANSITION METAL CHEMISTRY

MICHAEL F. LAPPERT and ROBERT S. ROWE
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (U.K.)
(Received 12 June 1989)

CONTENTS

A. INTRODUCTION AND CLASSIFICATION OF COMPLEXES

This article is concerned with the role of heavy group 14 element carbene analogues MX_2 in transition metal (M′) chemistry (M = Ge, Sn or Pb; $\overline{X}$ is a bulky monohapto ligand: $X = CHR_2$, NR_2, $OAr^{R'}$ or SAr^{Bu^t}; R = $SiMe_3$, $Ar^{R'} = C_6H_2Bu^t_2$-2,6-R′-4, R′ = H, Me or Bu^t). Various types of complexes, many of them containing an M′–M bond, may result from reactions between the germylene, stannylene or plumbylene MX_2 and the transition metal compound $L_nM'–X'$, as illustrated in Scheme 1. Thus MX_2 may behave in one of seven principal ways, designated Type 1 to Type 7: MX_2 may act as either a terminal (Type 1) or bridging (Type 2) ligand; it may insert into an M′–X′ bond thus generating the new ligand $\overline{M}X_2X'$ (Type 3); it may behave as an *N*-centred nucleophile with respect to a compound containing an M′–H bond, thus generating a new MX_2 species in which $X = M'L_n$ (Type 4); it may act as an $\overline{X}$ transfer reagent (Type 5); if $X = NR_2$ (R = $SiMe_3$), it may oxidatively add to a low oxidation state M′ centre by virtue of a C–H bond in $M(NR_2)_2$ with concomitant cyclometallation (Type 6); or it may function as a reducing agent (Type 7).

In Tables 1 and 2 we summarize data on transition metal complexes derived from various MX_2 precursors; typical syntheses are illustrated in Schemes 1–9 and eqns. (1)–(4).

There have been three reviews dealing with transition metal complexes based on MX_2 [1–3], of which two have dealt explicitly with the role of

0010-8545/90/$9.10

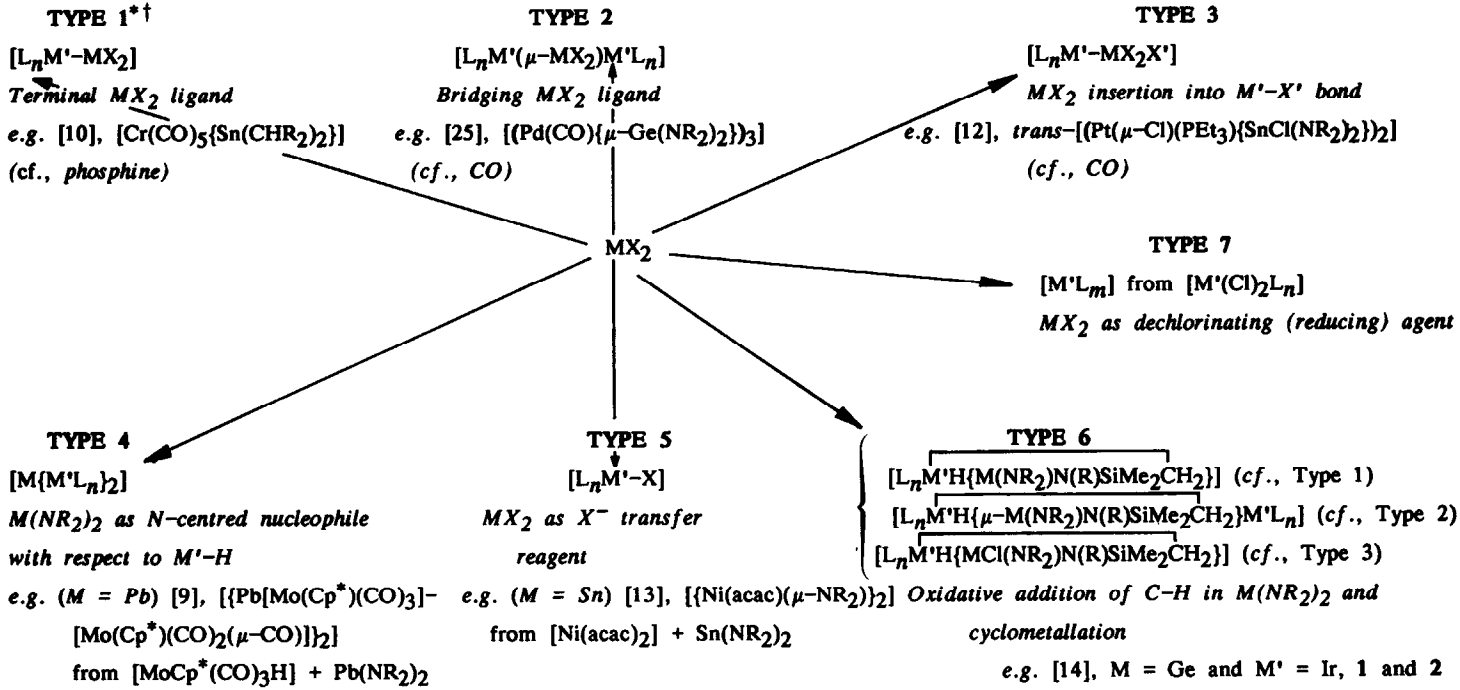
MX_2 as precursors for their complexes with transition metals [1,2]. Excluded from Tables 1 and 2 are complexes containing (i) $SnHal_2$, e.g. $[SnCl_2\{Co(CO)_4\}_2]$ [16]; (ii) $\bar{S}nHal_3$, e.g. $[PtCl(PEt_3)_2(SnCl_3)]$ and their germanium(II) or lead(II) analogues [17]; and (iii) a base adduct, e.g. $[Cr(CO)_5\{GeBr_2(NMe_3)\}]$ [18]; these are well documented elsewhere [3,19] and fall outside the scope of the present work. Also excluded are complexes (iv) prepared from an M(IV) precursor (M = Ge, Sn or Pb) by either reduction, e.g. $[Fe(CO)_4\{SnPh_2(THF)\}]$ [20], or oxidative addition, e.g. $[PtCl(PPh_3)_2\{Sn(CH_2Ph)_2Cl\}]$ [21]; (v) containing a polymeric group 14 metal-centred ligand, e.g. $[W(CO)_5\{Sn(OH)_2\}]_n$ [22]; and (vi) containing a porphyrinato–M ligand, e.g. $[Mn(CO)_5(\mu\text{-Hg})Mn(CO)_4\{Sn(tpp)\}]$ (tpp = tetraphenylporphinato) [58]. Some exceptions to the exclusions (i)–(vi) are made for X-ray characterized complexes.

The sole monomeric MX_2 precursors ($\bar{X}$ being a monohapto ligand) which have been used as sources of transition metal complexes have been those in which $X = CHR_2$ (a monomer in solution), NR_2, $OAr^{R'}$ or SAr^{Bu^t} (R = $SiMe_3$; $Ar^{R'} = C_6H_2Bu^t_2$-2,6-R′-4, R′ = H, Me or Bu^t). Apart from the work by Cardin and collaborators (Scheme 8), such chemistry has emerged exclusively from our laboratory. (Added in proof: The paper by Veith, Stahl and Huch [81] reports on rhodium(I) complexes of $\overline{SnN(Bu^t)SiMe_2NBu^t}$ in which there is unusual Cl^- bridging of adjacent tin atoms.)

The first heavy group 14 element carbene analogue ("metylene")-derived transition metal complex was $[Cr(CO)_5\{MX_2(THF)\}]$ ($MX_2 = GeMe_2$, $SnMe_2$ or $SnBu^t_2$), obtained in 1971 [7]. Such a complex is classified in Tables 1 and 2 as being of Type 1′. Related complexes may have the base stabilization provided by intramolecular neutral donor ligation, with M being in either a four-coordinate environment, as in $[Cr(CO)_5\{\overline{Sn(SCH_2CH_2)_2NBu^t}\}]$ [6], or a five-coordinate environment, as in $[Pt(PPh_3)_2\{Sn(acac)_2\}]$ (acacH = $MeCOCH_2COMe$) [8]. The first Type 1 complex derived directly from an MX_2 precursor was $[Cr(CO)_5\{Sn(CHR_2)_2\}]$ (R = $SiMe_3$) [28], reported in 1974. A rather special case of a complex bearing a terminal MX_2 ligand is one in which there is a short bond between a ligand attached to the transition metal and M; we refer to this as a Type 1″ complex, and it is exemplified by *cis*-$[Rh(Cl)(PPh_3)_2\{Sn(NR_2)_2\}]$ in which there is a close Cl · · · Sn interaction; this was described in 1988 [68].

There are several complexes having MX_2 as a bridging ligand; the atom M can then be regarded as having become tetravalent. The Type 2 complexes $[(M'(CO)\{\mu\text{-}M(NR_2)_2\})_3]$ (M′ = Pd or Pt, M = Ge or Sn) were reported in 1985 [70]; they were obtained by treating the appropriate Type 1 precursor $[M'\{M(NR_2)_2\}_3]$ with carbon monoxide.

A coordinated MX_2 moiety may not only be stabilized by a neutral but



Scheme 1. The role of the heavy group 14 element carbene analogues MX_2 (M = Ge, Sn or Pb; $\overline{X}$ is a monohapto ligand) in transition metal (M′) chemistry. Abbreviations: R = $SiMe_3$, Cp* = η-C_5Me_5, L_n = the sum of all other ligands within the coordination sphere of M′. * Type 1′ refers to a complex containing a neutral base-stabilized terminal MX_2 ligand, e.g. $[Cr(CO)_5\{Sn(Bu^t)_2(py)\}]$ [7]. † Type 1″ refers to a chloro-transition metal complex containing a terminal MX_2 ligand in which the Cl^- is semi-bridging (short Cl···M distance), e.g. *cis*-$[Rh(Cl)(PPh_3)_2\{Sn(NR_2)_2\}]$ [68].

TABLE 1

Transition metal (M′) complexes containing $M(NR_2)_2$ (M = Ge, Sn or Pb; R = $SiMe_3$) or a derivative

Complex [a]	Type	Comments	M′–M (Å)	Ref.
$[Sc(\eta\text{-}C_5H_5)_2Me\{Sn(NR_2)_2\}]$	1	IR, ^1H NMR		1
$[M'(CO)_5\{M(NR_2)_2\}]$ (M′ = Cr, Mo or W; M = Ge or Sn)	1	IR, ^1H NMR		1
trans-$[M'(CO)_4\{M(NR_2)_2\}_2]$ (M′ = Mo or W; M = Ge or Sn)	1	IR, ^1H NMR		1
$[W(CO)_5\{\overline{Sn(C_{10}H_6NMe_2\text{-}1,8)_2}\}]$	1′	IR, ^1H NMR, X-ray; five-coordinate Sn	2.822(1)	82
$[Mn(CO)_5\{SnBr(NR_2)_2\}]$	3	IR, ^1H NMR		1
$[Fe(\eta - C_5H_5)(CO)_2\{Sn(NR_2)_2X\}]$ (X = F, I or Me)	3	IR, ^1H NMR		1, 4
$[Rh(\eta\text{-PhMe})(\eta\text{-}C_2H_4)\{SnCl(NR_2)_2\}]$	3	^1H NMR, X-ray	2.5637(8)	23
$[Rh(\eta\text{-ArH})(\eta\text{-alkene})\{SnCl(NR_2)_2\}_2]$ (alkene = *trans*-hex-3-ene, ArH = PhMe; alkene = C_8H_{14} [b], ArH = C_6H_6, PhMe [b] or $C_6H_3Me_3$ − 2,4,6)	3	^1H NMR, X-ray	2.554(1)	24
$[(Rh(\mu\text{-Cl})\{Sn(NR_2)_2\}_2)_2]$	1	^1H NMR		24
$[Rh(cod)(L^{Me})\{SnMe(NR_2)_2\}]$	3	^1H, ^{13}C and ^{119}Sn NMR		68
$[Rh(cod)(L^{Me})\{SnCl(NR_2)_2\}]$	3	IR, ^1H, ^{13}C and ^{119}Sn NMR, X-ray	2.685(1)	68
$[Rh(cod)(PEt_3)\{SnCl(NR_2)_2\}]$	3	^1H, ^{13}C, ^{31}P and ^{119}Sn NMR, X-ray	2.647(1)	68
$[Rh(cod)(\{Sn(NR_2)_2\}_2(\mu\text{-Cl}))]$	3	IR, ^1H, ^{13}C and ^{119}Sn NMR; singly bridging Cl^-		68
$[(Rh(cod)\{\mu\text{-}Sn(NR_2)_2\}\{SnCl(NR_2)_2\})_2]$	2, 3	^1H, ^{13}C and ^{119}Sn NMR		68
cis-$[RhCl\{Ge(NR_2)_2\}(PPh_3)_2]$	1″ [c]	^1H and ^{31}P NMR, X-ray (semi-bridging Cl^-; Ge···Cl, 2. 723(4) Å)	2.39(1)	68
cis-$[Rh\{Sn(NBu^t)_2SiMe_2\}(\mu\text{-Cl}, Sn, Sn)(PPh_3)_2]$	1, 3	^1H and ^{31}P NMR, X-ray; Cl^- bridges the two tin atoms	2.576(2)	81

$[Rh\{Sn(NBu^t)_2SiMe_2\}_5(\mu\text{-Cl}, Sn, Sn)]$	1, 3	^1H and ^{31}P NMR, X-ray; trigonal bipyramidal Rh; Cl^- bridges two tin atoms	2.526(1)–2.568(1)	81
$[Rh(CO)(dppe)\{SnCl(NR_2)_2\}]$	3	IR, ^1H, ^{13}C, ^{31}P, ^{29}Si and ^{119}Sn NMR		68
cis-$[RhCl(PPh_3)_2\{Sn(NR_2)_2\}]$	1″ [c]	^1H and ^{31}P NMR, X-ray (semi-bridging Cl^-; Sn···Cl, 2.743(3) Å)	2.564(1)	23, 68
trans-$[Rh(CO)(PPh_3)_2\{SnCl(NR_2)_2\}]$	3	IR and ^{119}Sn NMR		68
$[Ir\{SnCl(NR_2)N(R)SiMe_2CH_2\}(cod)H\{Sn(NR_2)_2\}]$	3/6	IR, ^1H, ^{13}C and ^{119}Sn NMR		68
$[\{CH_2Me_2SiN(R)(NR_2)Ge\}HIr(\mu\text{-Cl})_2\text{-}\{Ge(NR_2)N(R)SiMe_2CH_2\}IrH\{Ge(NR_2)_2\}]$	1/6 2/6 1	^1H NMR, X-ray	2.325(3) $2.468(3)_{av}$ 2.331(3)	14
$[Ir\{GeCl(NR_2)N(R)SiMe_2CH_2\}(CO)_2H\text{-}\{Ge(NR_2)_2\}]$	1, 3/6 1	^1H NMR, X-ray	2.460(1) 2.418(1)	14
cis-$[Pd(\eta\text{-}C_3H_5)Cl\{M(NR_2)_2\}]$ (M = Sn or Pb)	1	^1H NMR		1
trans-$[Pd(CNBu^t)_2\{SnCl(NR_2)_2\}_2]$	3	^1H NMR, X-ray	2.636(1)	13
$[Pt\{M(NR_2)_2\}(PPh_3)_2]$ (M = Ge or Sn)	1	^1H, ^{31}P, ^{195}Pt and (for M = Sn; no py adduct) ^{119}Sn NMR		68
cis-$[Pt(cod)\{SnCl(NR_2)_2\}_2]$	3	^1H NMR		1
$[(Pt(\mu\text{-Cl})\{MCl(NR_2)_2\}(PEt_3))_2]$ (M = Ge, Sn [b] or Pb; *cis* or *trans* [b])	3	^{31}P NMR, X-ray	2.534(1)	1, 12
$[M'\{M(NR_2)_2\}_3]$ (M′ = Pd, M = Ge or Sn [b]; M′ = Pt, M = Ge or Sn [b])	1, 7(Pd)	^{195}Pt and ^{119}Sn NMR, X-ray	$2.53(1)_{av}$ $2.487(6)_{av}$	5, 12
$[(M'(CO)\{\mu\text{-}Sn(NR_2)_2\})_3]$ (M′ = Pd, M = Ge or Sn [b]; M′ = Pt, M = Ge or Sn [b])	1	^{195}Pt and ^{119}Sn NMR, X-ray	$2.621(5)_{av}$ $2.620(4)_{av}$	25, 70

[a] Abbreviations: R = $SiMe_3$, L^{Me} = :$\overline{CN(Me)(CH_2)_2NMe}$ and cod = cycloocta-1,5-diene.

[b] Designates those of the series which have been X-ray characterized.

[c] Type 1″ refers to a complex having a terminal MX_2 ligand, but in which there is also M···ClM′ semi-bridging.

TABLE 2

Transition metal (M′) complexes containing group 14 metal (M)-centred ligands other than $M(NR_2)_2$ (M = Ge, Sn or Pb; R = $SiMe_3$)

Complex [a]	Type	Comments	M′–M (Å)	Ref.
$[Cr(CO)_5\{Ge(C_6H_2Me_3\text{-}2,4,6)_2(L)\}]$ (L = absent or THF)	1, 1′ [c]	IR, ^1H NMR		26
$[M'(CO)_5\{M(CHR_2)_2\}]$ (M′ = Cr, M = Ge or Sn [b]; M′ = Mo, M = Sn or Pb)	1	IR, ^1H NMR, ^{119}Sn Mössbauer, X-ray	2.562(5)	10, 27, 28
trans-$[M'(CO)_4\{M(CHR_2)_2\}_2]$ (M′ = Cr, M = Ge; M′ = Cr or Mo, M = Sn)	1	IR, ^1H NMR, ^{119}Sn Mössbauer		10, 29
$[Mo(\eta\text{-}C_5H_5)(CO)_3\{Sn(CHR_2)_2X\}]$ (X = H or Me)	3	IR, ^1H NMR, ^{119}Sn Mössbauer		10, 28
$[W(CO)_2(S_2CNR'_2)_2\{Sn(CHR_2)_2\}]$ (R′ = Me or Et)	1	IR, ^1H and ^{119}Sn NMR		69
$[Cr(CO)_5\{Sn(Bu^t)_2(py)\}]$	1′ [c]	IR, ^1H NMR, ^{119}Sn Mössbauer, X-ray (Sn^{IV} precursor)	2.653(3)	7
$[M'(CO)_5\{M(\eta\text{-}C_5Me_5)Cl\}]$ (M′ = Cr, M = Ge or Sn; M′ = W, M = Ge [b] or Sn)	1	IR, ^1H and ^{13}C NMR, X-ray	2.511(1)	31, 32
$[W(CO)_5\{Ge(\eta\text{-}C_5Me_5)R'\}]$ (R′ = Me, CHR_2 [b] or NR_2)	1	IR, ^1H, ^{13}C and ^{29}Si NMR, X-ray	2.632(2)	31
$[M'(CO)_5\{Ge(\eta\text{-}C_5H_5)Cl(THF)\}]$ (M′ = Cr or W)	1′ [c]	IR, ^1H NMR		32
$[Cr(\eta\text{-}C_5H_5)(CO)_3(SnPh_3)]$	3	IR, ^1H NMR, X-ray	2.85	33
$[M'(CO)_5\{Ge(NPh_2)_2(L)\}]$ (M′ = Cr, L = absent; M′ = W, L = absent, py or $HNPh_2$)	1′ [c]	IR, ^1H NMR		18
$[W(CO)_5\{Ge(NPr^i_2)Cl(py)\}]$	1′ [c]	IR, ^1H NMR		18
$[(M'(CO)_5\{Sn(\mu\text{-}NMe_2)(NMe_2)\})_2]$ (M′ = Cr, Mo or W)	1′ [c]	IR (monomeric THF adduct exists in THF solution)		34
$[M'(CO)_5\{Sn(NBu^t)_2SiMe_2\}]$ (M′ = Cr, Mo or W)	1	IR, ^1H NMR		35
$[Cr(CO)_5\{Ge(SR')_2(L)\}]$ (R′ = Me, Et, Ph or CH_2Ph, L = absent or N=S(CH)C_6H_4-4)	1, 1′ [c]	IR, ^1H NMR		36, 37
$[M'(CO)_5\{Ge(SC_6H_2Me_3\text{-}2,4,6)_2(L)\}]$ (M′ = Cr, L = absent [b], NMe_3, py, PPh_3 or N=S(CH)C_6H_4-4; M′ = W, L = absent)	1, 1′ [c]	IR, ^1H NMR, X-ray	2.367(2)	18, 36, 37
$[Cr(CO)_5\{Sn(SCH_2CH_2)_2NBu^t\}]$	1′ [c]	IR, ^1H and ^{13}C NMR, X-ray	2.622(1)	7

$[Cr(CO)_5\{Sn(SC_6H_2Bu^t_3-2,4,6)_2\}]$	1	IR, ^1H NMR		38, 79
$[(M'(CO)_5\{SnCl(\mu\text{-}SBu^t)\})_2]$ (M' = Cr or W)	1′ [c]			39
$[Cr(CO)_5\{Sn(SCH_2CH_2)_2PPh\}]$	1′ [c]	^{13}C, ^{31}P and ^{119}Sn NMR		41
$[W(CO)_5\{Sn(SCH_2CH_2)_2X(L)\}]$ (X = O, S or NMe, L = absent or py; X = NBu′, L = absent)	1′ [c]	IR, ^1H, ^{13}C, ^{15}N and ^{119}Sn NMR		40
$[W(CO)_5\{Sn(C_6H_2Bu^t_3\text{-}2,4,6)_2\}]$	1	IR, ^1H NMR		79
$[W(CO)_5\{Sn(C_6H_4PPh_2\text{-}2)_2\}]$	1′ [c]	^{13}C, ^{31}P and ^{119}Sn NMR, ^{119}Sn Mössbauer		42
$[(M'(CO)_5\{Sn(\mu\text{-}OCH_2CH_2N(R')CH_2CH_2O)\})_2]$ (M' = Cr, Mo or W; R′ = Me or Bu′)	1′ [c]	IR, ^1H, ^{13}C, ^{15}N and ^{119}Sn NMR		40
$[M'(CO)_5\{Sn(NCS)_2\}]$ (M' = Cr or W)	1	IR		43, 44
$[M'(CO)_5\{M(OCOCH_3)_2[O(COCH_3)_2]\}]$ (M' = Cr, Mo or W; M = Sn or Pb)	1′ [c]	IR		43–45
$[M'(CO)_5\{Sn(OH)_2(THF)\}]$ (M' = Cr or W)	1′ [c]	IR, ^{119}Sn NMR, stable in THF solution (base-free species is polymeric)		22
$[M'(CO)_5\{Sn[OC(NMe_2)]_2Fe(CO)_4\}]$ (M' = Cr, Mo or W)	1′ [c]	IR, ^1H and ^{13}C NMR		34
$[(Cr(CO)_5\{Sn(\mu\text{-}OSiMe_3)(OSiMe_3)\})_2]$	1′ [c]	IR		46
$[(W(CO)_5\{Sn(\mu\text{-}OSiPh_3)(OSiPh_3)\})_2]$	1′ [c]	IR, ^{13}C and ^{11y}Sn NMR		46
$[M'(CO)_5(Sn\{OC(R')CHC(R'')O\}_2)]$ (M' = Cr, Mo or W, R′ = R″ = Me or CF_3, or R′ = Me and R″ = Ph, or R′ = Me and R″ = CF_3)	1′ [c]	IR, ^1H and ^{19}F NMR		47, 48
$[W(CO)_5\{M[W(CO)_5]_2(L)\}]$ (M = Ge L = absent [b]; M = Sn, L = absent [b] or THF [b])	1/4	IR, X-ray (shortest W–M distances); M^{IV} precursor	2.505(2) 2.702(2) 2.713(2)	49, 50
$[Sn\{M'(CO)_5\}_2]$ (M' = Cr or W)	4	IR, linear M′–Sn–M′ array; Sn^{IV} precursor		43, 51
$[Pb\{Mo(R')(CO)_3\}_2(L)]$ (R′ = η-C_5H_5, η-$C_5H_3(SiMe_3)_2$-1,3 or η-C_5Me_5 [b]; L = absent or THF)	4′ [c], 4	IR, X-ray; base-free species[d] is dimeric in the solid state	2.935(1)[d] 2.989(1)[d] 2.989(2) 3.019(2)	9
$[M'(\eta\text{-}C_5H_5)(CO)_3\{Sn(PR'_2)_2CX\}]$ (M' = Mo, R′ = Me, X = $SiMe_3$; M′ = W, R′ = Ph, X = PPh_2)	4′ [c]	^{31}P and ^{119}Sn NMR		52

TABLE 2 (continued)

Complex [a]	Type	Comments	M′–M (Å)	Ref.
$[Mn(\eta\text{-}C_5H_4Me)(CO)_2(\overline{Sn\{OC(R')CHC(R'')O\}_2})]$ ($R' = R'' =$ Me, CF_3 or Ph; R' = Me and R'' = Ph or CF_3)	1′ [c]	IR		53
$[Mn(\eta\text{-}C_5H_4R')(CO)_2(M\{Mn(\eta\text{-}C_5H_4R')(CO)_2\}_2)]$ (M = Ge, R' = H [b] or Me [b]; M = Sn, R' = Me [b]; M = Pb, R' = Me [b])	1/4	IR, X-ray (shortest Mn–M distances); M^{IV} precursor	2.250(1) 2.260(2) 2.424(8) 2.490(1)	54–57
$[M\{Mn(\eta\text{-}C_5R'_4R'')(CO)_2\}_2]$ (M = Ge, R' = H, R'' = Me [b] or R' = R'' = Me [b]; M = Pb, and R' = R'' = H [b])	4	IR, X-ray, linear Mn–M–Mn array; M^{IV} precursor	2.204(1) 2.18(2) 2.463(1)	54, 55, 59, 60
$[Fe(\eta\text{-}C_5H_5)(CO)(\mu\text{-}CO)_2Fe(\eta\text{-}C_5H_5)\{Sn(CHR_2)_2\}]$	1	IR		10(a), 28
$[Fe(\eta\text{-}C_5H_5)(CO)_2\{Sn(CHR_2)_2X\}]$ (X = F, Cl, Br, I, OMe, H or Me)	3	IR, ^{1}H and ^{119}Sn NMR, ^{119}Sn Mössbauer		10, 28, 30
$[Os_3Sn(\mu\text{-}H)_2(CO)_{10}(CHR_2)_2]$	1′ [c]	Ir, ^{1}H NMR, X-ray	2.658(1)	61
$[\{Fe(CO)_4\}_2\{\mu\text{-}Sn(CHR_2)_2\}]$	2	IR, ^{1}H NMR, ^{119}Sn Mössbauer		10, 11, 28
$[(Fe(CO)_3\{\mu\text{-}Sn(CHR_2)_2\})_2]$	2	X-ray, details unpublished		11
$[M'_3(CO)_9(\mu\text{-}CO)\{\mu\text{-}Sn(CHR_2)_2\}_2]$ (M' = Ru [b] or Os [b])	2	X-ray	$2.735(2)_{av}$ $2.732(7)_{av}$	11
$[Os_3(CO)_8(\mu\text{-dppm})\{\mu\text{-}Sn(CHR_2)_2\}_2]$	2	IR, X-ray, asymmetric Sn bridges	$2.870(3)_{av}$ $2.650(3)_{av}$	62
$[Fe(CO)_4\{M(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2\}]$ (M = Ge [b] or Sn [b])	1	IR, ^{1}H NMR, X-ray	2.240(2) 2.408(1)	63
$[Fe(CO)_4(\overline{Sn\{OC(R')CHC(R'')O\}_2}(py))]$ (R' = Me, R'' = Ph or CF_3; R' = R'' = CF_3)	1′ [c]	IR, ^{57}Fe Mössbauer		48
$[\{Fe(CO)_4\}_2(\mu\text{-}\overline{Sn\{OC(Me)CHC(Ph)O\}_2})]$	2′ [c]	IR		64

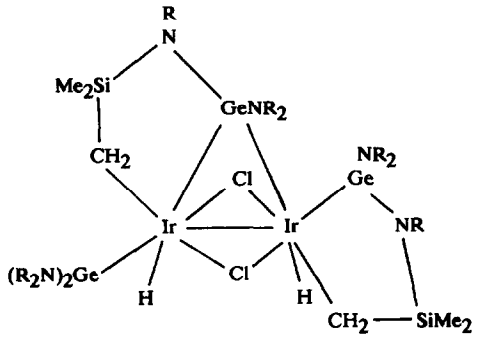
$[Fe(CO)_4(Sn\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(L))]$ (L = absent [b], THF or py [b])	1/4	IR, ^1H, ^{13}C and ^{119}Sn NMR, X-ray(isocarbonyl-bridged dimer in the solid state)[d] (shortest Fe–Sn distances); Sn^{IV} precursor	2.527(1) [d] 2.581(1)	69
$[Cr(CO)_5(Sn\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2)]$	1/4	IR, ^1H and ^{13}C NMR, X-ray (isocarbonyl-bridged dimer in the solid state) [c]; Sn^{IV} precursor	2.624(1) (Cr) 2.570(1) (Fe) 2.550(2) (Fe)	69
$[Ge\{Co(CO)_4\}X]$ (X = F or $Co(CO)_4$)	4	IR, trapping with 1,3-dimethyl-buta-1,3-diene		65
cis-$[RhCl(PPh_3)_2\{Sn(CHR_2)_2\}]$	1	^1H, ^{31}P and ^{119}Sn NMR		10(a), 28, 68
cis-$[RhCl(PPh_3)_2\{Sn(OC_6H_3Bu^t_2\text{-}2,6)_2\}]$	1	^1H and ^{31}P NMR		68
$[PtCl(PEt_3)\{Sn(CHR_2)_2\}(SnCl(CHR_2)_2\}]$ (*cis* or *trans*)	1, 3	IR, ^1H and ^{31}P NMR, ^{119}Sn Mössbauer		10, 22, 28
trans-$[(Pt(\mu\text{-}Cl)(PEt_3)\{SnCl(CHR_2)_2\})_2]$	3	^{31}P NMR		22
$[Ni(CO)_3\{Sn(\mu\text{-}OSiMe_3)(OSiMe_3)\}_2]$	1′ [c]	IR		46
$[(Ni(CO)_3\{M(\mu\text{-}OBu^t)(OBu^t)\})_2]$ (M = Ge [b] or Sn)	1′ [c]	IR, ^{13}C and ^{119}Sn NMR, X-ray	2.283(2)	46, 66
$[Pt(PPh_3)_2\{Sn(acac)_2\}_2]$	1′ [c]	^{31}P, ^{119}Sn and ^{195}Pt NMR, X-ray	$2.558(1)_{av}$	8
$[Pt_2(PPh_3)_2\{\mu\text{-}Sn(acac)_2\}_3]$	2′ [c]	^{31}P, ^{119}Sn and ^{195}Pt NMR, X-ray	$2.680(1)_{av}$	8
$[PtH(PEt_3)(SnR'_2\{\mu\text{-}O(R'')SnR'_2\}_2)(SnR'_3)]$ (R′ = C_6H_4Me-4, R″ = H or Me [b])	1′ [c], 3	IR, ^1H, ^{31}P and ^{119}Sn NMR, X-ray	2.616(1)	67
$[Pt(CO)_2\{Sn(CHR_2)_2\}_2]$	1	IR, ^1H, ^{13}C and ^{195}Pt NMR		15
$[Pt(PPh_3)_2\{Sn(OC_6H_3Bu^t_2\text{-}2,6)_2\}]$	1	^1H, ^{31}P and ^{195}Pt NMR		68

[a] Abbreviations: R = $SiMe_3$, Ar = $C_6H_2Bu^t_2$-2,6-Me-4, acacH = $MeCOCH_2COMe$, dppm = $(Ph_2P)_2CH_2$.
[b] Designates those of the series which have been X-ray characterized.
[c] Types 1′, 2′ or 4′ refer to the appropriate (see types 1, 2 or 4 respectively) transition metal (M′) base-stabilized MX_2 complex.
[d] Base-free species.

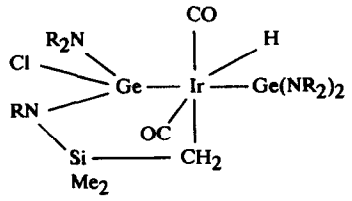
also by an anionic base $\overline{X}'$; the ligand $\overline{M}X_2X'$ results from insertion of MX_2 into a transition metal (M′) M′–X′ bond. The first such Type 3 complex derived from an MX_2 precursor was $[Mo(\eta\text{-}C_5H_5)(CO)_3\{Sn(CHR_2)_2X\}]$ (X = H or Me), described in 1974 [28].

Attempts have been made to obtain a dimetallastannylene or dimetallaplumbylene MX_2 in which $X = M'L_n$ (Type 4 behaviour). The only compounds that have been made and well characterized to date in which the metal M has an open-shell configuration are the lead(II) species of Scheme 5; the crystalline complexes have three-coordinated lead, and included $Pb[MoCp^*(CO)_3]_2(THF)$ (there is evidence for the isoleptic Sn compound [75]) and $\{Pb[MoCp^*(CO)_3]_2\}_2$ ($Cp^* = \eta\text{-}C_5Me_5$); they were reported in 1987 [9]. Other two- or three-coordinate main group 14 metal–$M'L_n$ complexes are known in which M is in oxidation state +4, such as compounds **3** or **4** ([Mn] = $[Mn(\eta\text{-}C_5H_4Me)(CO)_2]$) [54]. It is not inevitable that complexes of type $[M(M'L_n)_3]$ have a cyclic three-membered $\overline{M'MM'}$ ring structure; indeed acyclic analogues have been made, one of which (see Fig. 1) is of mixed-metal type [69].

As the ligand $\overline{X}$ in MX_2 is in principle capable of acting as a leaving group, it is possible that a compound MX_2 may behave as an $\overline{X}$ transfer reagent (Type 5 behaviour). The reaction between the tin(II) amide and $[Ni(acac)_2]$, illustrated in Scheme 1, was established in 1987 [13].

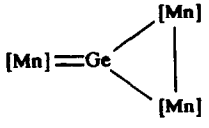


1



2

3



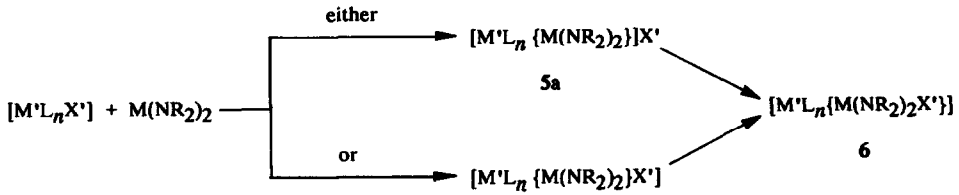
4

Compound **1** is made from $[\{Ir(\eta\text{-}C_8H_{14})_2(\mu\text{-}Cl)\}_2]$ and $Ge(NR_2)_2$; treating **1** with carbon monoxide generates a further complex, **2**; both exemplify Type 6 behaviour, as noted in 1986 [14].

That a metylene may function as a chlorine-atom-abstracting reagent (Type 7 behaviour) in a transition metal context was first observed in 1985 [12]; thus $[Sn(CHR_2)_2Cl]_2$ was one of the products isolated from $[\{PtCl(\mu\text{-}Cl)(PEt_3)\}_2]$ and $Sn(CHR_2)_2$.

B. SYNTHESIS OF METYLENE-BASED TRANSITION METAL COMPLEXES

Typical reactions of a metylene MX_2 with a transition metal substrate $[M'L_nX']$ are illustrated in Schemes 2–8. The most intensively studied reactions refer to the amides $M(NR_2)_2$ ($R = SiMe_3$). In Scheme 2 selected $[M'L_nX']$ substrates are shown with M′ ranging from a group 3 to a group 10 transition metal, in low or high oxidation state. It is envisaged that the reaction pathway leading to any product of Scheme 2 invariably involves an initial Type 1 complex **5**; however, **5** may undergo rearrangement to yield the Type 3 isomer **6**, as a result of a 1,2-shift of an anionic ligand $\overline{X}$ from the outer or inner coordination sphere of the transition metal M′ to M (eqn. (1)):



(1)

The transformation $M(NR_2)_2 \rightarrow$ **6** is a carbene-like (or CO-like) insertion of MX_2 into an M′–X′ bond. The $M(NR_2)_2$ reactions leading to **5** or **6** demonstrate the ability of MX_2 to act as a metal-centred nucleophile or substrate for insertion (Type 1 or Type 3 behaviour respectively). The former mode shows that MX_2 has a transition metal reactivity analogous to that of a tertiary phosphine or carbon monoxide.

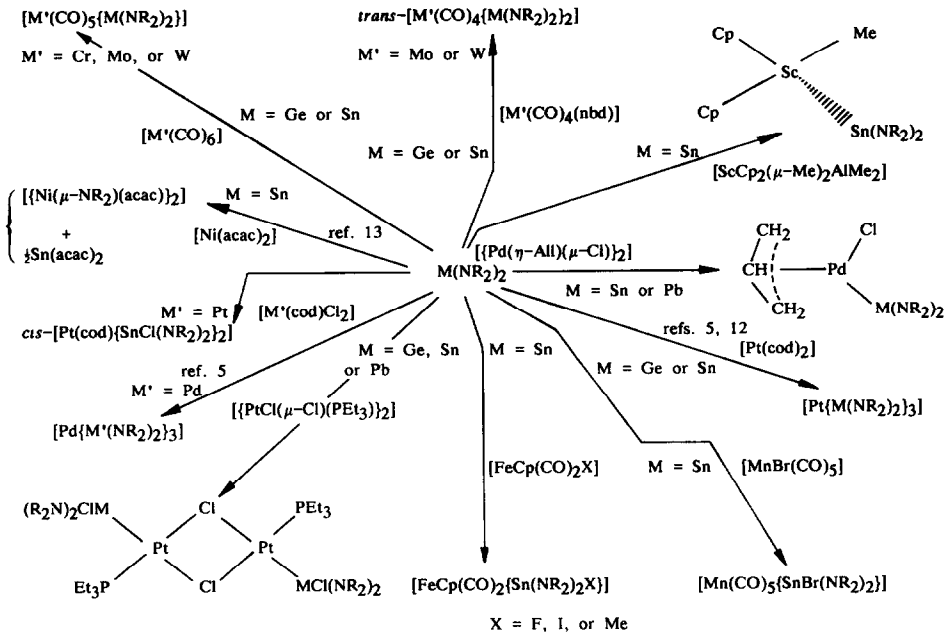
The fact that MX_2 may function as a bridging ligand (Type 2 behaviour) shows a further analogy with CO. The metylene MX_2 in its Type 2 reaction may also be considered as acting as a reducing agent, in the sense that an M(II) precursor is converted into an M(IV) product. A clearer example of MX_2 as a reducing agent, although concomitantly as a ligand, is illustrated in eqn. (2) [70]:

$$[Pd(cod)Cl_2] \xrightarrow[M = Ge \text{ or } Sn]{4M(NR_2)_2} [Pd\{M(NR_2)_2\}_3] \qquad (2)$$

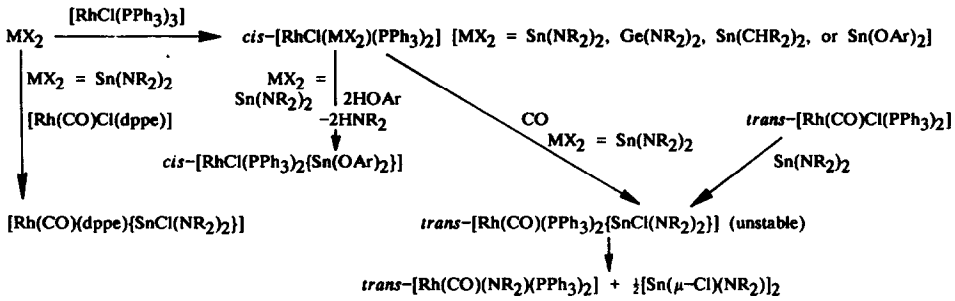
A germanium or tin amide $M(NR_2)_2$ may function as an addendum for oxidative addition to a low oxidation state transition metal substrate (cf. $H\overset{\delta+}{—}\overset{\delta-}{A}$ oxidative addition and cyclometallation) whereby MX_2 gives rise to a new hybrid bidentate ligand such as $R_2N(Cl)\overline{M}N(R)SiMe_2\overline{C}H_2$ or $R_2N\ddot{M}N(R)SiMe_2\overline{C}H_2$, each of which may behave in either a bridging or a chelating fashion (see **1** and **2** [14]). A further example of such Type 6 behaviour is shown in eqn. (3) [68]:

$$\tfrac{1}{2}[\{Ir(cod)(\mu\text{-}Cl)\}_2] \xrightarrow[\text{ref. 68}]{2Sn(NR_2)_2} [\overline{Ir\{SnCl(NR_2)N(R)SiMe_2CH_2\}}(cod)H\{Sn(NR_2)_2\}] \quad (3)$$

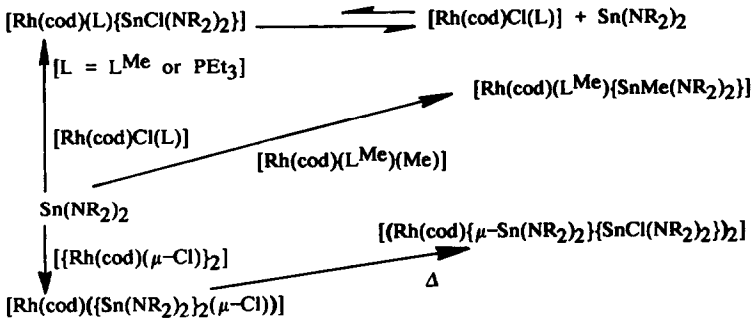
Routes to dimetallaplumbylene complexes from $Pb(NR_2)_2$ are illustrated in Scheme 5 [9]. Of the compounds listed, two have been X-ray characterized, $Pb[MoCp^*(CO)_3]_2(THF)$ and $\{Pb[MoCp^*(CO)_3][MoCp^*(CO)_2(\mu\text{-}CO)]\}_2$ (*O*, *Pb*) ($Cp^* = \eta\text{-}C_5Me_5$; $THF = OC_4H_8$), both of which contain a three-coordinate lead atom. In the latter compound there are unusual isocarbonyl–Pb bonds, as illustrated in Fig. 2. Attempts to make the tin



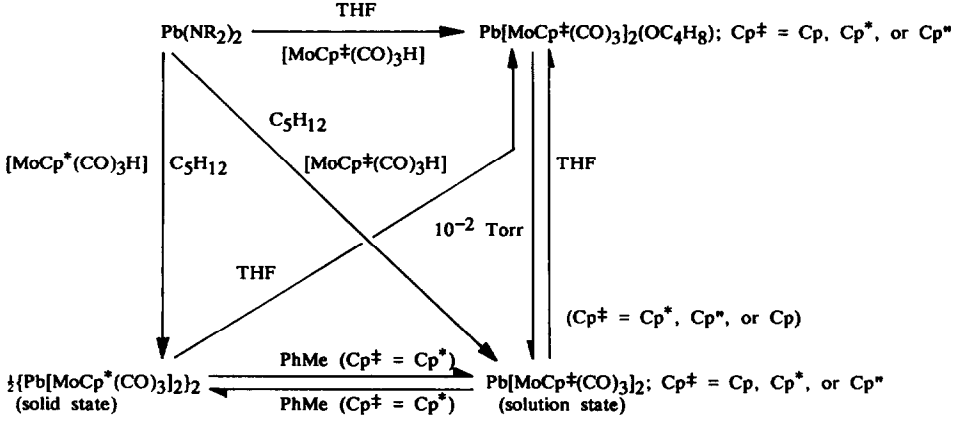
Scheme 2. Some transition metal (M′) reactions of $M(NR_2)_2$ ($R = SiMe_3$, $Cp = \eta\text{-}C_5H_5$, $All = \eta\text{-}C_3H_5$, nbd = norbornadiene, cod = cycloocta-1,5-diene, acacH = acetylacetone) (from ref. 1 unless otherwise stated).



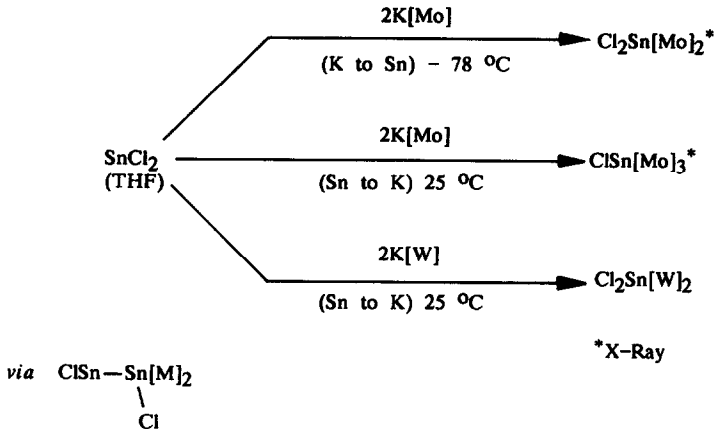
Scheme 3. Some phosphinerhodium(I) complexes derived from MX_2 ($MX_2 = Sn(NR_2)_2$, $Ge(NR_2)_2$, $Sn(CHR_2)_2$ or $Sn(OAr)_2$; dppe = $(Ph_2PCH_2)_2$, R = $SiMe_3$, Ar = $C_6H_3Bu^t_2$-2,6) [68].



Scheme 4. Some cycloocta-1,5-dienerhodium(I) complexes derived from $Sn(NR_2)_2$ (R = $SiMe_3$, $L^{Me} = :\overline{CN(Me)(CH_2)_2NMe}$) [68].



Scheme 5. Routes to some Pb(II)–Mo(0) complexes from $[MoCp^‡(CO)_3H]$ and $Pb(NR_2)_2$ (R = $SiMe_3$, Cp = η-C_5H_5, Cp* = η-C_5Me_5, Cp" = η-$C_5H_3R_2$-1,3) [9].



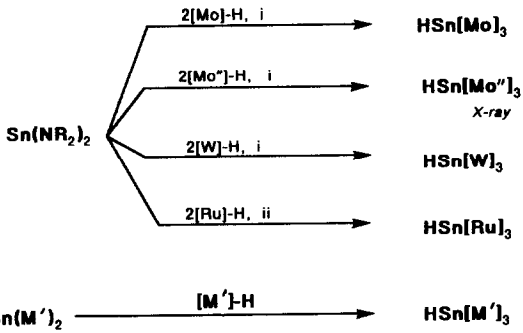
Scheme 6. Interaction of $SnCl_2$ and $[MCp(CO)_3]^-$ (M = Mo or W, [Mo] = $[MoCp(CO)_3]$, [W] = $[WCp(CO)_3]$) [75].

analogue from $Sn(NR_2)_2$ (R = $SiMe_3$) failed, probably because the intermediate dimetallastannylene was unstable with regard to oxidative addition; the isolated compounds were the hydridotrimetallatin(IV) complexes (Scheme 7) [75]. Alternative efforts at generating the dimetallatin(II) complexes from $SnCl_2$ likewise led to tin(IV) products (Scheme 6); in this case the reaction pathway might well have also involved a transient dimetallastannylene which rapidly underwent insertion into one of the Sn–Cl bonds of $SnCl_2$.

A similar type of isocarbonyl–metal interaction has been found in some polycarbonylchromium(0) and polycarbonyl-iron(0) complexes in which $Sn[FeCp(CO)_2]_2$ (abbreviated as $SnFp_2$) may be considered as the putative dimetallastannylene intermediate [69]; details are shown in Scheme 9.

C. REACTIONS

Various reactions of a complex containing a coordinated stannylene or stannate(II) anion are shown in Schemes 3, 5 and 9. These include the conversion of a rhodium(I)-coordinated $Sn(NR_2)_2$ complex to the corresponding $Sn(OAr)_2$ derivative by treatment of the former with the phenol ArOH (Ar = $C_6H_3Bu^t_2$-2,6). Such a reaction represents a nucleophilic displacement at tin in a Type 1 complex. Similar nucleophilic substitutions, but in Type 3 complexes, are illustrated in eqn. (4) (X′ = F (via $[NBu^n_4]F$), OMe (via NaOMe) or H (via $K[BHEt_3]$)) [30]. $[FeCp(CO)_2\{Sn(CHR_2)_2H\}]$ underwent H/Cl exchange at tin by reaction with aqueous HCl or PhCOCl

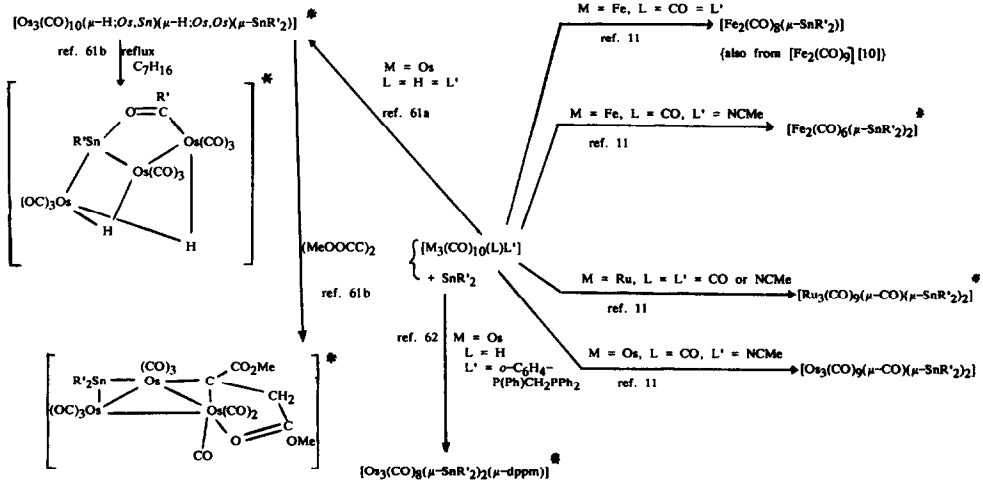


Scheme 7. Interaction of $Sn(NR_2)_2$ ($R = SiMe_3$) and a transition metal hydride $[M'Cp(CO)_3H]$ ($M' = Mo$ or W), $[Mo(\eta\text{-}C_5H_3R_2\text{-}1,3)(CO)_3H]$ or $[RuCp(CO)_2H]$ (abbreviated as [M']-H, [Mo"]-H and [Ru]-H respectively). Reaction conditions: i, C_6H_{14}, 25 °C; ii, C_7H_{16}, reflux [75].

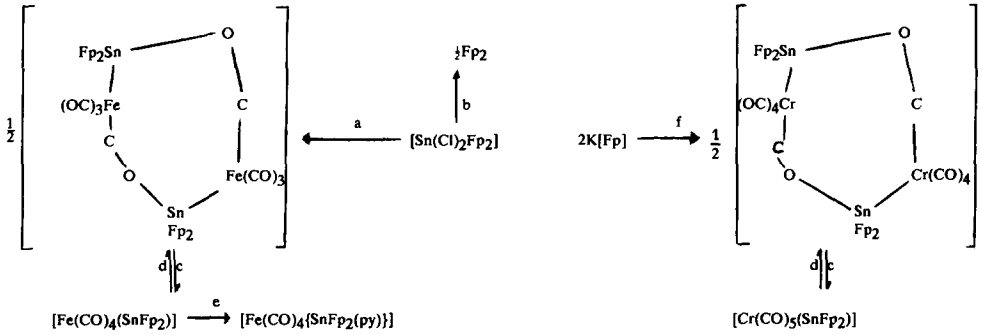
(also yielding PhCHO) [30]:

$$[FeCp(CO)_2\{Sn(CHR_2)_2I\}] \xrightarrow[\text{ref. 30}]{\bar{X}'} [FeCp(CO)_2\{Sn(CHR_2)_2X'\}] \qquad (4)$$

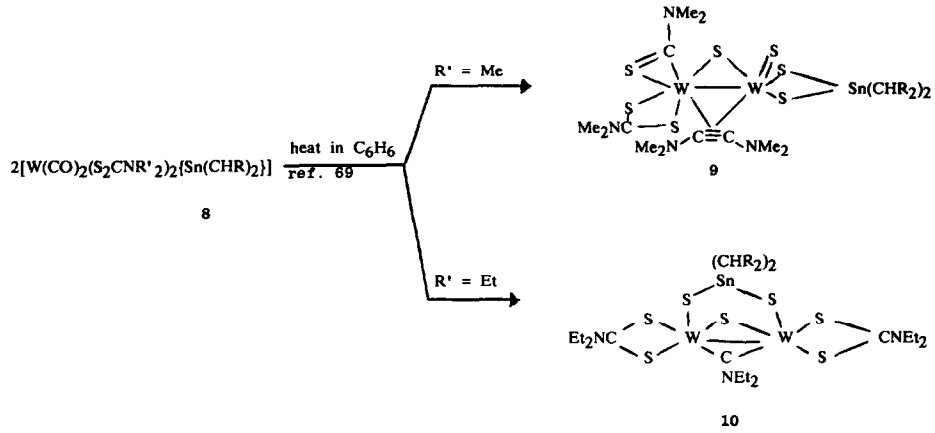
The conversion of a Type 1 complex into a Type 2 complex by reaction of the former with CO has already been cited in the context of the transformation of $[M'\{M(NR_2)_2\}_3]$ into $[(M'\{\mu\text{-}M(NR_2)_2\}(CO))_3]$ (7) ($M' = Pd$ or Pt, M = Ge or Sn) [15,25,70]. Likewise the Type 1/6 complex **1** was converted with CO into the Type 3/6 complex **2** [14].



Scheme 8. Reactions of SnR'_2 ($R' = CHR_2$, $R = SiMe_3$, dppm = $Ph_2PCH_2PPh_2$ with some carbonyltrimetallic clusters of Fe, Ru or Os [11,61(a),61(b),62]; * X-ray.



Scheme 9. Some polycarbonylchromium(0) and polycarbonyliron(0) $SnFp_2$ complexes (Fp = $[Fe(\eta\text{-}C_5H_5)(CO)_2]$) [69]. Reagents: a, $Na_2[Fe(CO)_4]\cdot 1,5$-dioxane; b, $Na_2[Cr(CO)_5]$; c, PhMe; d, $-$PhMe; e, py; f, $[Cr(CO)_5\{SnCl_2(THF)\}]$.



8 9 10

The complexes **7** underwent reversible one-electron electrochemical reduction in tetrahydrofuran at approximately -1.2 V to yield ESR-characterized reduction products containing, in the case of the tin compounds, a Pd_nSn_2 or Pt_3Sn_3 core [25]. This was established by analysis of their frozen solution ESR spectra, the samples being generated by controlled potential electrolysis of **7** in the cavity of the spectrometer.

The dithiocarbamatotungsten(II) complexes **8**, containing a dialkylstannylene ligand, were partially desulphurized to yield the remarkable X-ray characterized complexes **9** and **10** (eqn. (5)) [69].

D. STRUCTURE AND BONDING

The X-ray structures of some representative complexes are shown in Figs. 1–7. These include two examples showing the metylene ligand functioning in

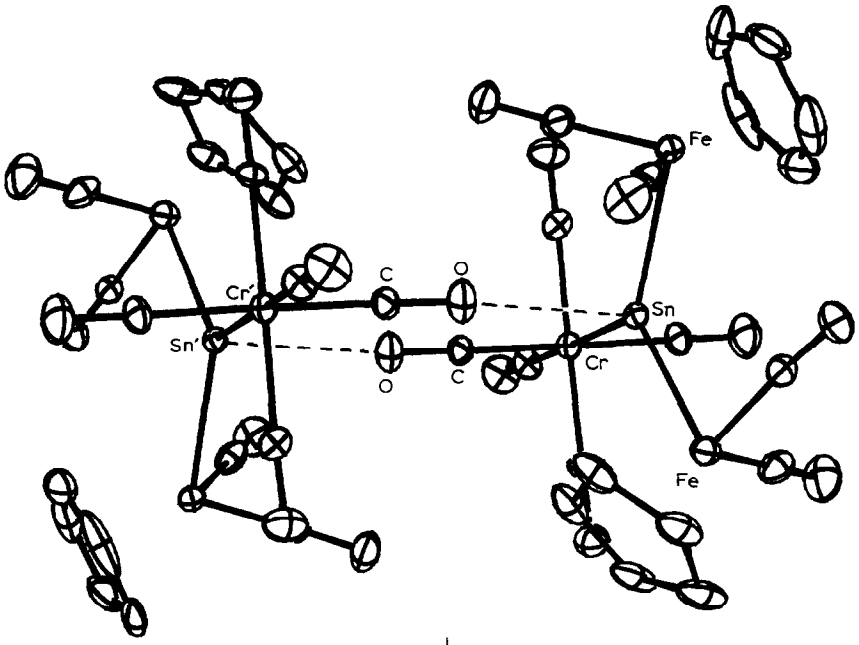


Fig. 1. X-ray structure of $[\{Cr(CO)_4(\mu\text{-}CO)\}(SnFp_2)]_2$. 2PhMe (*O,Cr*) (toluene solvent not shown: $Fp = [Fe(\eta\text{-}C_5H_5)(CO)_2]$) [69]. Selected structural data: Cr–Sn 2.624(1) Å, Fe–Sn 2.570 (1) and 2.550(2) Å, Sn–O 2.976(7) Å, Cr–CO(μ) 1.862(9) Å, μ-C–O 1.166(2) Å; Cr–Sn–Fe 121.81(5)° and 121.46(4)°, Fe–Sn–Fe 115.74(4)°, O–Sn–Cr 98.5(1)°, Sn–O–C 169.4(7)°, Cr–C–O(μ) 176.9(6)°.

a Type 1 fashion (Figs. 1 and 5). Figure 3 illustrates the structures of two Type 1″ complexes [76,77]; although these are formally of structure *cis*-$[RhCl\{M(NR_2)_2\}(PPh_3)_2]$, they nevertheless reveal a rather close Cl · · · M (M = Ge or Sn) interaction. Figures 4 and 6 exemplify structures of Type 3 complexes, while Fig. 7 refers to one of Type 2. X-ray data on a Type 4 complex are shown in Fig. 2 and similar information is also available for the Type 6 species **1** and **2** [14].

From Table 2 it is evident that X-ray data are available on complexes other than those having a bis(amido)metylene precursor, including $M(CHR_2)_2$ and $M(OAr^{Me})_2$ ($R = SiMe_3$, $Ar^{Me} = C_6H_2Bu^t_2$-2,6-Me-4).

In Table 3 selected results are given on some typical $[M'(MX_2)L_n]$ complexes having $X = CHR_2$, NR_2 or OAr^{Me}; for comparison similar data are provided on the parent monomeric metylene MX_2. It can be noted that there is no monotonic trend in either the XMX angle or the M–X bond length as between MX_2 and $[M'L_n(MX_2)]$.

^{119}Sn NMR chemical shifts of various SnX_2-derived complexes are listed in Table 4. They are of considerable diagnostic value, although no interpretation of these data is proposed at this time.

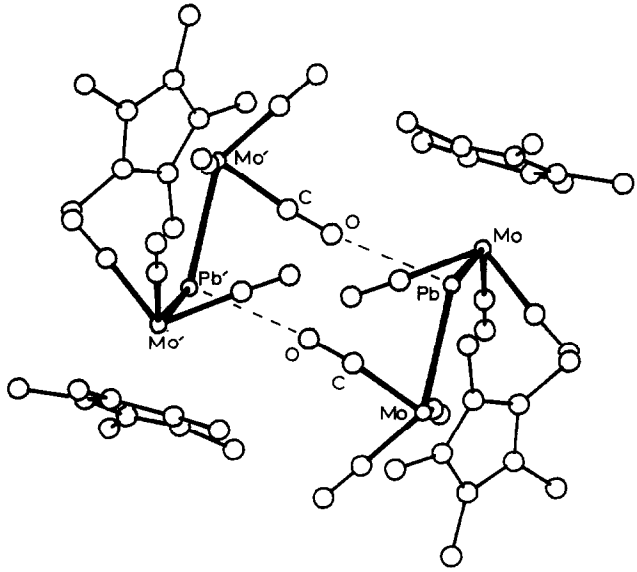


Fig. 2. X-ray structure of $\{Pb[MoCp^*(CO)_3][MoCp^*(CO)_2(\mu\text{-}CO)]\}_2$ (*O,Pb*) ($Cp^* = \eta\text{-}C_5Me_5$) [9]. Selected structural data: Mo–Pb 2.935(1) and 2.989(1) Å, Pb–O 2.918(8) Å; Mo–Pb–Mo 120.71(2)°.

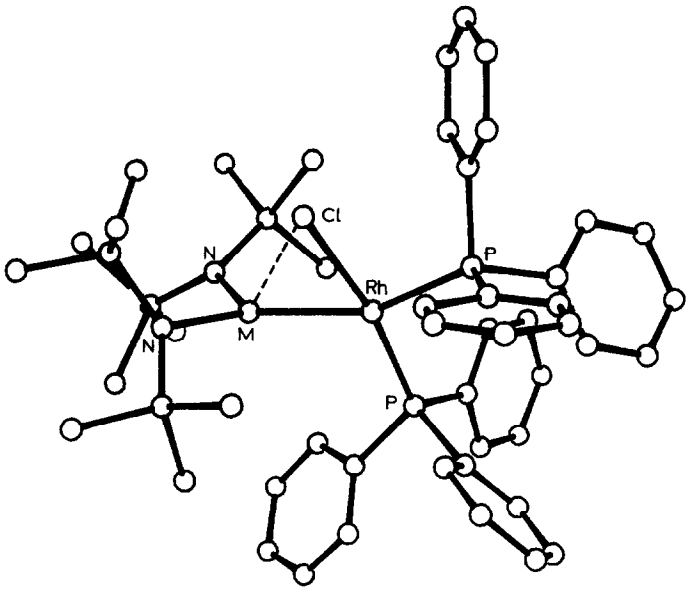


Fig. 3. X-ray structure of *cis*-$[RhCl\{M(NR_2)_2\}(PPh_3)_2]$ (M = Ge [76] or Sn [77], R = $SiMe_3$) [68]. Selected structural data for M = Ge (M = Sn in parentheses): Rh–M 2.391(1) (2.564(1)) Å, Rh–Cl 2.388(3) (2.418(3)) Å, Rh–P 2.218(3) and 2.335(3) (2.210(2) and 2.296(3)) Å, M–N 1.881(8) and 1.849(9) (2.085(7) and 2.058(7)) Å, M···Cl 2.723(4) (2.743(3)) Å; M–Rh–Cl 69.46(9)° (66.74(6)°), M–Rh–P 103.47(9)° and 157.42(9)° (103.46(7)° and 156.83(7)°), Cl–Rh–P 170.9(1)° and 88.5(1)° (168.86(9)° and 90.64(9)°), P–Rh–P 99.0(1)° (99.51(9)°), Rh–M···Cl 55.23(7)° (54.07(5)°), N–M···Cl 119.8(3)° and 91.3(3)° (117.9(2)° and 91.9(2)°).

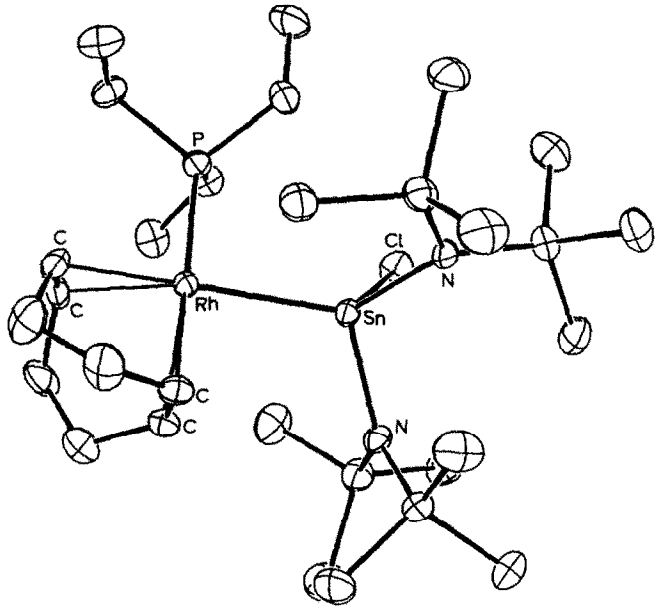


Fig. 4. X-ray structure of $[Rh(cod)(PEt_3)\{SnCl(NR_2)_2\}]$ ($R = SiMe_3$) [68,78]. Selected structural data: Rh–Sn 2.647(1) Å, Rh–P 2.318(1) Å, Rh–C 2.180(5), 2.189(5), 2.229(5) and 2.252(5) Å, Sn–Cl 2.449(1) Å, Sn–N 2.120(4) and 2.099(4) Å; Sn–Rh–P 91.3(1)°, P–Rh–C 89.3(1)°, 96.0(1)°, 167.0(2)° and 157.1(1)°, Rh–Sn–N 113.7(1)° and 123.6(1)°, Rh–Sn–Cl 114.5(1)°, Cl–Sn–N 96.3(1)° and 95.3(1)°, N–Sn–N 108.7(1)°.

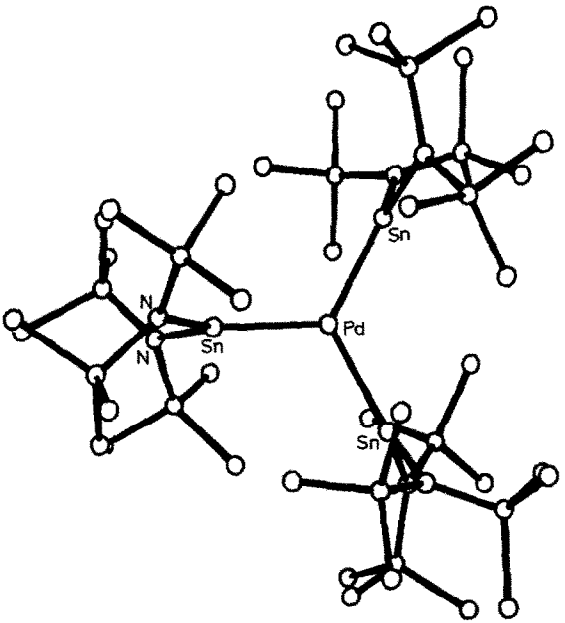


Fig. 5. X-ray structure of $[Pd\{Sn(NR_2)_2\}_3]$ ($R = SiMe_3$) [70]. Selected structural data: Pd–Sn 2.533(1), 2.540(1) and 2.517(1) Å; Sn–Pd–Sn 118.82(4)°, 120.78(4)° and 120.40(4)°.

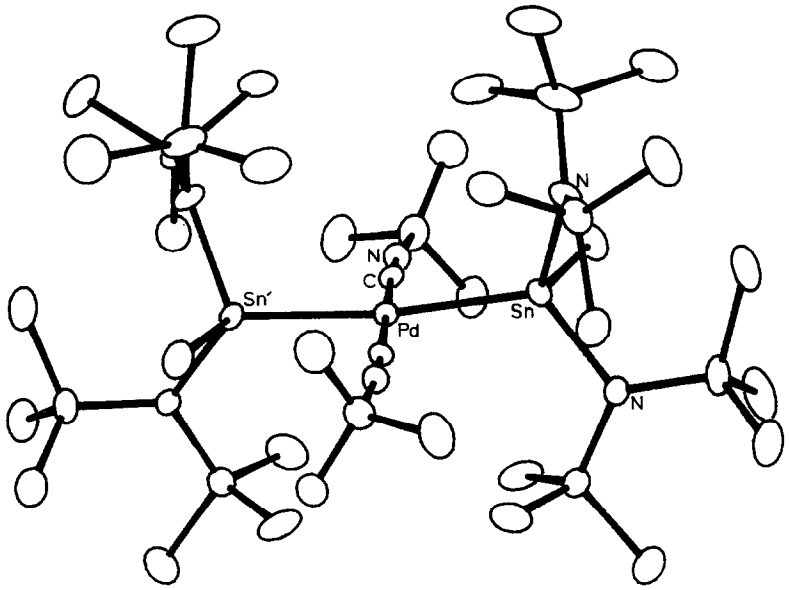


Fig. 6. X-ray structure of *trans*-$[Pd(CNBu^t)_2\{SnCl(NR_2)_2\}_2]$ ($R = SiMe_3$) [13]. Selected structural data: Pd–Sn 2.636(1) Å, Pd–C 1.978(1) Å, Sn–N 2.083(7) and 2.075(8) Å. Sn–Cl 2.406(3) Å; Pd–Sn–Cl 112.57(7)°, Pd–Sn–N 121.9(2)° and 109.9(3)°, Cl–Sn–N 93.9(2)° and 100.1(2)°.

TABLE 3

Comparative structural data for selected group 14 metal(II) compounds MX_2 and some of their transition metal complexes (A) [a]

Compound MX_2 or (A)	XMX (deg)	⟨M–X⟩ (Å)	Ref.
GeR'_2	107(2) [b]	2.04(2) [b]	71
SnR'_2	97(2) [b]	2.22(2) [b]	71
$[Cr(CO)_5(GeR'_2)]$	102.8(2)	1.98(2)	27
$[Cr(CO)_5(SnR'_2)]$	98	2.18(1)	10(a)
$Ge(NR_2)_2$	101(1.5) [b]	1.89(1) [b]	72
$Sn(NR_2)_2$	96 [b], 104.7(2)	2.09(1) [b], 2.09(1)	73
$[Pd\{Sn(NR_2)_2\}_3]$	107(1)	2.08(2)	70
$[Pt\{Sn(NR_2)_2\}_3]$	104(1)	2.1(2)	12
$Ge(OAr)_2$	92.0(4)	1.80(2)	74
$Sn(OAr)_2$	88.4(2)	2.01(2)	74
eq-$[Fe(CO)_4\{Ge(OAr)_2\}]$	93.5(2)	1.777(8)	63
eq-$[Fe(CO)_4\{Sn(OAr)_2\}]$	92.2(2)	1.974(15)	63

[a] Abbreviations: $R' = CHR_2$, $R = SiMe_3$, $Ar = C_6H_2Bu^t_2$-2,6-Me-4.
[b] In the vapour (gas-phase electron diffraction); other data are for the crystal (X-ray).

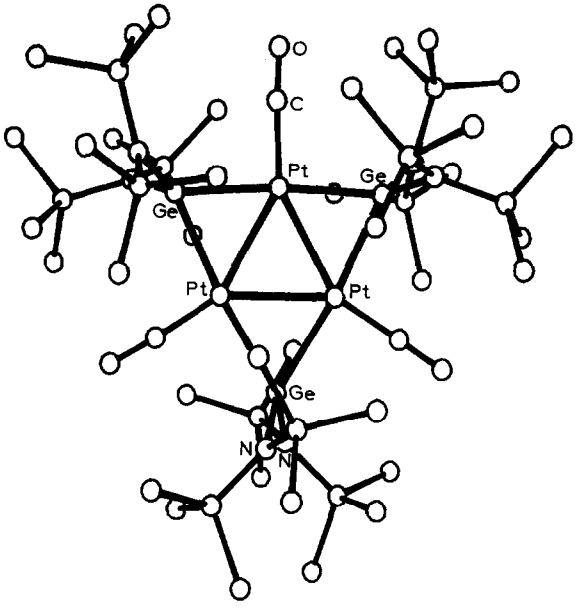


Fig. 7. X-ray structure of $[(Pt\{\mu\text{-}Ge(NR_2)_2\}(CO))_3]$ (R = $SiMe_3$) [15,80]. Selected structural data: Pt–Pt, 2.735(2), 2.727(2) and 2.723(2) Å, Pt–Ge 2.473(3), 2.482(3), 2.466(3), 2.481(3), 2.473(4) and 2.479(4) Å, Ge–N 1.87(2), 1.86(2), 1.89(2), 1.91(2), 1.88(2) and 1.93(2) Å, Pt–C 1.77(3), 1.78(3) and 1.88(3) Å.

From X-ray, NMR and IR data it is clear that in Type 1 complexes the MX_2 ligand can be regarded as being not only an effective σ donor, but also a powerful π acceptor. This is consistent with the complexes $[Fe(CO)_4\{M(OAr^{Me})_2\}]$ (M = Ge or Sn) having the MX_2 ligand in the equatorial position in their trigonal bipyramidal structure [63]. They have the MO_2 plane of $M(OAr^{Me})_2$ tilted from the $Fe(CO)_{axial}M$ plane by only 4.9° for M = Ge or 5.2° for M = Sn. Likewise in octahedral complexes, including $[Cr(CO)_5\{Sn(CHR_2)_2\}]$, the conformation of the MX_2 ligand is such as to maximize the possibility of π bonding to the transition metal (the plane containing the methine carbon atoms, tin and chromium is coplanar with the mutually axial COs and the CO *trans* to tin) [10].

From X-ray data for some rhodium(I) complexes, the relative *trans* influence appears to be $L^{Me} \approx PEt_3 > \bar{S}nCl(NR_2)_2 \gg \bar{C}l$ (L^{Me} = $:\overline{CN(Me)(CH_2)_2NMe}$) [68].

ACKNOWLEDGEMENTS

M.F.L. is grateful to the colleagues cited in the references for their effective collaboration. We thank the S.E.R.C. and B.P. Chemicals Plc (Hull) for the award of a CASE studentship to R.S.R., and Dr. D.J. Gulliver for his interest.

TABLE 4

^{119}Sn NMR data [a] for transition metal complexes containing tin-centred ligands derived from a stannylene SnX_2

Compound	$\delta(^{119}Sn)$		$\Delta\delta_L$	$^1J(M', ^{119}Sn)$ [k]	Sn coordination		Hybridization at Sn	Ref.
	Complex	Ligand			No.	"Type" [l]		
$[Fe(Cp)(CO)_2(SnR'_2X')]$								
$X' = F$ [g]	322	721 [m]	−399	–	4	3	sp^3	30
$X' = Cl$ [g]	311	721 [m]	−410	–	4	3	sp^3	30
$X' = Br$ [h]	292	721 [m]	−429	–	4	3	sp^3	30
$X' = I$ [d]	228	721 [m]	−493	–	4	3	sp^3	30
$X' = OMe$ [g]	267	721 [m]	−454	–	4	3	sp^3	30
$X' = H$ [g]	35	721 [m]	−686	–	4	3	sp^3	30
$[Fe(CO)_4(Sn\{Fe(Cp)(CO)_2\}_2)]$	724	(535 [n])	–	–	3	1	sp^2	69
$[Fe(CO)_4(Sn\{Fe(Cp)(CO)_2\}_2(THF)_x)]$ [i]	888	(535 [n])	–	–	$3+x$	1′	sp^2	69
$[Fe(CO)_4(Sn\{Fe(Cp)(CO)_2\}_2(py))]$ [h]	762	(535 [n])	–	–	4	1′	sp^2	69
$[W(CO)_2(S_2CNEt_2)_2(SnR'_2)]$ [g]	174	721 [m]	−547	–[o]	3	1	sp^2	69
$[W(CO)_2(S_2CNMe_2)_2(SnR'_2)]$ [g]	188	721 [m]	−533	–[o]	3	1	sp^2	69
cis-$[RhCl(PPh_3)_2(SnR'_2)]$ [j]	434	721 [m]	−287	497	3	3/6[t]	sp^2	68
$[Rh(CO)(dppe)\{SnCl(NR_2)_2\}]$ [j]	36	775	−739	739	4	3	sp^3	68
trans-$[Rh(CO)(PPh_3)_2\{SnCl(NR_2)_2\}]$ [j]	−60	775	−835	560	4	3	sp^3	68
$[Rh(cod)(L^{Me})\{SnMe(NR_2)_2\}]$ [j]	31	775	−744	815	4	3	sp^3	68

$[Rh(cod)(L^{Me})\{SnCl(NR_2)_2\}]$ [j]	−25	775	−800	– [p]	4	3	sp^3	68
$[Rh(cod)(PEt_3)\{SnCl(NR_2)_2\}]$ [j,c]	−12	775	−787	928	4	3	sp^3	68
$[Rh(cod)(\{Sn(NR_2)_2\}_2\{\mu\text{-}Cl\})]$ [j,d]	−4	775	−779	860	4	"3"	sp^3	68
$[(Rh(cod)\{\mu\text{-}Sn(NR_2)_2\}\text{-}$	144	775	−631	840	4	2	sp^3	68
$\{SnCl(NR_2)_2\})_2]$ [j,q]	118	775	−657	655	4	3	sp^3	68
$[Ir\{SnCl(NR_2)N(R)SiMe_2CH_2\}\text{-}$	−193	775	−968	–	4	3(6)[t]	sp^3	68
$(cod)H\{Sn(NR_2)_2\}]$ [j]	356	775	−419	–	3	1′	sp^2	68
$[(IrCl\{\mu\text{-}Sn(NR_2)_2\}\{Sn(NR_2)_2\})_2]$ [j,r]	221	775	−554	–	4	2	sp^3	68
	237	775	−538	–	3	1	sp^2	68
$[Pt(PPh_3)_2\{Sn(NR_2)_2\}]$ [h]	963	775	188	16650	3	1	sp^2	68
$[Pt\{Sn(NR_2)_2\}_3]$ [g,e]	885	775	110	27874	3	1	sp^2	70
$[Pd\{Sn(NR_2)_2\}_3]$ [g,e]	815	775	40	–	3	1	sp^2	70
$[Pt(PPh_3)_2\{Sn(acac)_2\}_2]$ [b,f]	−601	−702	101	12891	5	1′	$sp^3d(?)$[s]	8

Abbreviations: $R' = CHR_2$, $R = SiMe_3$, $L^{Me} = :\overline{CN(Me)(CH_2)_2}\overline{NMe}$; $\Delta\delta_L = \delta(\text{complex}) - \delta(\text{ligand})$.

[a] Recorded at 134.3 MHz except [b] 93.3 MHz, and at ambient temperature except [c] 273 K, [d] 193 K and [e] 343 K and [f] not reported; the following solvents were used: [g] benzene-d_6, [h] toluene-d_8, [i] THF-d_8 (presumably coordinated), [j] 10% toluene-d_8/toluene; δ in ppm relative to $SnMe_4$, positive shifts to higher frequency. [k] Coupling constants J in Hertz. [l] Types 1–6 are identified in Scheme 1. [m] Value reported for dimer in solution [18]. [n] Value for $[\{Fe(Cp)(CO)_2\}_2SnCl_2]$ [15]; $[\{Fe(Cp)(CO)_2\}_2Sn]$ is not known. [o] Not observed. [p] Not resolved. [q] Relative assignment based on coupling patterns. [r] Structure tentatively assigned on the basis of limited data on crude sample. [s] Not reported. [t] The Type 6 ligand $\bar{S}nCl(NR_2)N(R)SiMe_2CH_2^-$ is inserted into the Ir–Cl bond, so the Sn environment is essentially Type 3

REFERENCES

1 M.F. Lappert and P.P. Power, J. Chem. Soc., Dalton Trans., (1985) 51.
2 M.F. Lappert, Rev. Silicon, Germanium, Tin Lead Compd., 9 (1986) 129; Chem. Abstr., 107 (1986) 23372g.
3 W. Petz, Chem. Rev., 86 (1986) 1019.
4 D.H. Harris and M.F. Lappert, J. Chem. Soc., Chem. Commun., (1974) 895.
5 P.B. Hitchcock, M.F. Lappert and M.C. Misra, J. Chem. Soc., Chem. Commun., (1985) 863.
6 A. Tzschach, K. Jurkschat, M. Scheer, J. Meunier-Piret and M.J. van Meerssche, J. Organomet. Chem., 259 (1983) 165.
7 T.J. Marks, J. Am. Chem. Soc., 93 (1971) 7090.
M.D. Brice and F.A. Cotton, J. Am. Chem. Soc., 95 (1973) 4529.
8 G.W. Bushnell, D.T. Eadie, A. Pidcock, A.R. Sam, R.D. Holmes-Smith, S.R. Stobart, E.T. Brennan and T.S. Cameron, J. Am. Chem. Soc., 104 (1982) 5837.
9 P.B. Hitchcock, M.F. Lappert and M.J. Michalczyk, J. Chem. Soc., Dalton Trans., (1987) 2635.
10 (a) J.D. Cotton, P.J. Davidson and M.F. Lappert, J. Chem. Soc., Dalton Trans., (1976) 2275.
(b) J.D. Cotton, P.J. Davidson, M.F. Lappert, J.D. Donaldson and J. Silver, J. Chem. Soc., Dalton Trans., (1976) 2286.
11 C.J. Cardin, D.J. Cardin, G.A. Lawless, J.M. Power and M.B. Power, J. Organomet. Chem., 325 (1987) 203.
12 T.A.K. Al-Allaf, C. Eaborn, P.B. Hitchcock, M.F. Lappert and A. Pidcock, J. Chem. Soc., Chem. Commun., (1985) 548.
13 E. Arpac, P.B. Hitchcock, H.A. Jasim, M.F. Lappert and L. Linford, unpublished results, 1987.
14 S.M. Hawkins, P.B. Hitchcock, M.F. Lappert and A.K. Rai, J. Chem. Soc., Chem. Commun., (1986) 1689.
15 M.C. Misra, D. Phil. Thesis, University of Sussex, 1986.
16 D.J. Patmore and W.A. Graham, Inorg. Chem., 5 (1966) 1405.
17 P.S. Pregosin and S.N. Sze, Helv. Chim. Acta., 61 (1978) 1848.
18 P. Jutzi, W. Steiner and K. Stroppel, Chem. Ber., 113 (1980) 3357.
19 K.M. MacKay and B.K. Nicholson, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 6, Pergamon, Oxford, 1982, pp. 1043–1114.
20 T.J. Marks and A.R. Newman, J. Am. Chem. Soc., 95 (1973) 769.
G.W. Grynkewich, B.Y.K. Ho, T.J. Marks, D.L. Tomaja and J.J. Zuckerman, Inorg. Chem., 12 (1973) 2522.
21 G. Butler, C. Eaborn and A. Pidcock, J. Organomet. Chem., 181 (1979) 47.
22 W.-W. du Mont and B. Neudert, Angew. Chem., Int. Ed. Engl., 19 (1980) 553.
23 S.M. Hawkins, D. Phil. Thesis, University of Sussex, 1985.
24 S.M. Hawkins, P.B. Hitchcock and M.F. Lappert, J. Chem. Soc., Chem. Commun., (1985) 1592.
25 G.K. Campbell, P.B. Hitchcock, M.F. Lappert and M.C. Misra, J. Organomet. Chem., 289 (1985) C1.
26 P. Jutzi and W. Steiner, Angew. Chem., Int. Ed. Engl., 16 (1977) 639.
27 M.F. Lappert, S.J. Miles, P.P. Power, A.J. Carty and N.J. Taylor, J. Chem. Soc., Chem. Commun., (1977) 458.

28 J.D. Cotton, P.J. Davidson, D.E. Goldberg, M.F. Lappert and K.M. Thomas, J. Chem. Soc., Chem. Commun., (1974) 893.
29 M.F. Lappert, S.J. Miles and P.P. Power, J. Chem. Soc., Chem. Commun., (1977) 458.
30 P.B. Hitchcock, M.F. Lappert, M.J. McGeary and R.V. Parish, J. Organomet. Chem., 373 (1989) 107.
31 P. Jutzi, B. Hampel, M.B. Hursthouse and A.J. Howes, J. Organomet. Chem., 299 (1986) 19.
32 P. Jutzi, B. Hampel, K. Stroppel, C. Krüger, K. Angermund and P. Hofmann, Chem. Ber., 118 (1985) 2789.
33 Y.T. Struchkov, K.N. Anismov, O.P. Osipova, N.E. Kolobova and A.N. Nesmeyanov, Proc. Acad. Sci. USSR, 172 (1967) 15.
34 W. Petz, J. Organomet. Chem., 165 (1979) 199.
35 M. Veith, H. Lange, H. Braeuer and R. Bachmann, J. Organomet. Chem., 216 (1981) 377.
36 P. Jutzi, W. Steiner, E. Koenig, G. Huttner, A. Frank and U. Schubert, Chem. Ber., 111 (1978) 606.
37 P. Jutzi and W. Steiner, Angew. Chem., Int. Ed. Engl., 15 (1976) 684.
38 P.B. Hitchcock. M.F. Lappert, B.J. Samways and E.L. Weinberg, J. Chem. Soc., Chem. Commun., (1983) 1492.
39 W.-W. du Mont, cited in ref. 3.
40 A. Zschunke, M. Scheer, M. Voltzke, K. Jurkschat and A. Tzschach, J. Organomet. Chem., 308 (1986) 325.
41 U. Baumeister, H. Hartung, K. Jurkschat and A. Tzschach, J. Organomet. Chem., 304 (1986) 107.
42 K. Jurkschat, H.-P. Abicht, A. Tzschach and B. Mahieu, J. Organomet. Chem., 309 (1986) C47.
43 G.K.-I. Magomedov, L.V. Morozova, V.S. Nikitin, T.A. Shestakova and N.M. Bizyukova, J. Coord. Chem., 8 (1981) 558.
44 G.K.-I. Magomedov and L.V. Morozova, J. Gen. Chem. USSR, 51 (1981) 1967 (English translation).
45 G.K.-I. Magomedov, G.V. Druzhkova, Y.I. Markova and L.V. Morozova, J. Gen. Chem. USSR, 55 (1985) 815 (English translation).
46 M. Grenz and W.-W. du Mont, J. Organomet. Chem., 241 (1983) C5.
47 A.B. Cornwell and P.G. Harrison, J. Chem. Soc., Dalton Trans., (1975) 1486.
48 A.B. Cornwell, P.G. Harrison and J.A. Richards, J. Organomet. Chem., 76 (1974) C26.
49 G. Huttner, U. Weber, B. Sigwarth, O. Scheidsteger, H. Lang and L. Zsolnai, J. Organomet. Chem., 282 (1985) 331.
50 O. Schneidsteger, G. Huttner, K. Dehnicke and J. Pebler, Angew. Chem., Int. Ed. Engl., 24 (1985) 428.
51 G.K.-I. Magomedov, L.V. Morozova and Y.I. Markova, J. Gen. Chem. USSR, 53 (1983) 1515 (English translation).
52 H.H. Karsch and A. Appelt, J. Organomet. Chem., 312 (1986) C6.
53 A.B. Cornwell and P.G. Harrison, J. Chem. Soc., Dalton Trans., (1976) 1054.
54 W. Gäde and E. Weiss, J. Organomet. Chem., 213 (1981) 451.
55 D. Melzer and E. Weiss, J. Organomet. Chem., 263 (1984) 67.
56 W.A. Herrmann, Angew. Chem., Int. Ed. Engl., 25 (1986) 56.
57 W.A. Herrmann, H.-J. Kneuper and E. Herdtweck, J. Am. Chem. Soc., 109 (1987) 2508.
58 (a) S. Onaka, Y. Condo, K. Toriumi and T. Ito, Chem. Lett., (1980) 1605.
(b) S. Onaka, Y. Condo, M. Yamashita, Y. Tatematsu, Y. Kato, M. Goto and T. Ito, Inorg. Chem., 24 (1985) 1070.

59 (a) J.D. Korp, I. Bernal, R. Hörlein, R. Serrano and W.A. Herrmann, Chem. Ber., 118 (1985) 340.
(b) W.A. Herrmann, J. Weichmann, U. Küsthardt, A. Schäfer, R. Hörlein, C. Hecht, E. Voss and R. Serrano, Angew. Chem., Int. Ed. Engl., 22 (1983) 979.
60 W.A. Herrmann, H.-J. Kneuper and E. Herdtweck, Angew. Chem., Int. Ed. Engl., 24 (1985) 1062.
61 (a) C.J. Cardin, D.J. Cardin, H.E. Parge and J.M. Power, J. Chem. Soc., Chem. Commun., (1984) 609.
(b) C.J. Cardin, D.J. Cardin, J.M. Power and M.B. Hursthouse, J. Am. Chem. Soc., 107 (1985) 505.
62 R.A. Bartlett, C.J. Cardin, D.J. Cardin, G.A. Lawless, J.M. Power and P.P. Power, J. Chem. Soc., Chem. Commun., (1988) 312.
63 P.B. Hitchcock, M.F. Lappert, S.A. Thomas, A.J. Thorne, A.J. Carty and N.J. Taylor, J. Organomet. Chem., 315 (1986) 27.
64 A.B. Cornwell and P.G. Harrison, J. Chem. Soc., Dalton Trans., (1975) 2017.
65 A. Castel, P. Rivière, J. Satgé, J.J. Moreau and R.J.P. Corriu, Organometallics, 2 (1983) 1498.
66 M. Grenz, E. Hahn, W.-W. du Mont and J. Pickardt, Angew. Chem., Int. Ed. Engl., 23 (1984) 61.
67 J.F. Almeida, K.R. Dixon, C. Eaborn, P.B. Hitchcock, A. Pidcock and J. Vinaixa, J. Chem. Soc., Chem. Commun., (1982) 1315.
68 R.S. Rowe, D. Phil. Thesis, University of Sussex, 1988.
69 P.B. Hitchcock, M.F. Lappert and M.J. McGeary, unpublished results, 1988.
70 P.B. Hitchcock, M.F. Lappert and M.C. Misra, J. Chem. Soc., Chem. Commun., (1985) 863.
71 T. Fjeldberg, A. Haaland, B.E.R. Schilling, M.F. Lappert and A.J. Thorne, J. Chem. Soc., Dalton Trans., (1986) 1551.
72 T. Fjeldberg, H. Hope, M.F. Lappert, P.P. Power and A.J. Thorne, J. Chem. Soc., Chem. Commun., (1983) 639.
73 M.F. Lappert, P.P. Power, M.J. Slade, L. Hedberg, K. Hedberg and V. Schomaker, J. Chem. Soc., Chem. Commun., (1979) 369.
74 B. Çetinkaya, I. Gümrükçü, M.F. Lappert, J.L. Atwood, R.D. Rogers and M.J. Zaworotko, J. Am. Chem. Soc., 102 (1980) 2088.
75 P.B. Hitchcock, M.F. Lappert and M.J. Michalczyk, unpublished results, 1987.
76 P.B. Hitchcock, M.F. Lappert, R.S. Rowe and N. Sarjudeen, unpublished results, 1988.
77 R. Bohra, P.B. Hitchcock, M.F. Lappert and R.S. Rowe, unpublished results, 1988.
78 M.F. Lappert, G. Müller and R.S. Rowe, unpublished results, 1988.
79 M.F. Lappert, E.L. Weinberg and R.E. Taylor, unpublished results, 1986.
E.L. Weinberg, M.Phil. Thesis, University of Sussex, 1983.
R.E. Taylor, D.Phil. Thesis, University of Sussex, 1989.
80 P.B. Hitchcock, M.F. Lappert and M.C. Misra, unpublished results, 1987.
81 M. Veith, L. Stahl and V. Huch, Inorg. Chem., 28 (1989) 3278.
82 J.T.B.H. Jastrzebski, P.A. van der Schaaf, J. Boersma, G. van Koten, D. Heijdenrijk, K. Goubitz and D.J.A. de Ridder, J. Organomet. Chem., 367 (1989) 55.